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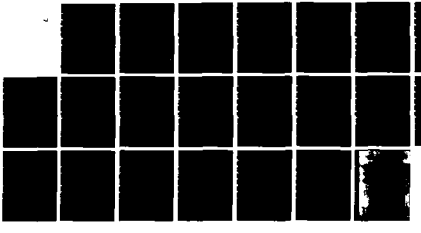
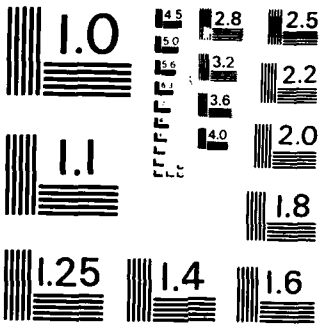
UNCLASSIFIED APR 84 TR-28 N00014-79-C-0670 F/G 7/4 NL





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OFFICE OF NAVAL RESEARCH

Contract N00014-79-0670

TECHNICAL REPORT NO. 28

Surface-Enhanced Raman Spectrocopy of Pentaammineosmium(III)/(II) and Pentaammineruthenium(II) Containing Pyridine, Pyrazine, or 4,4'-Bipyridine Ligands at Silver Electrodes: Vibrational Assignments

by

Stuart Farquharson, Peter A. Lay, and Michael J. Weaver

Prepared for Publication

in the

Spectrochim. Acta A.

Department of Chemistry

Purdue University

West Lafayette, IN 47907

April 1983

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: Technical Report No. 28	2. GOVT ACCESSION NO.: AD-A142439
	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): Surface-Enhanced Raman Spectroscopy of Pentaammineosmium(III)/(II) and Pentaammineruthenium(II) Containing Pyridine, Pyrazine, or 4,4'-Bipyridine Ligands at Silver Electrodes: Vibrational Assignments	5. TYPE OF REPORT & PERIOD COVERED: Technical Report No. 28
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Stuart Farquharson, Peter A. Lay, Michael J. Weaver	8. CONTRACT OR GRANT NUMBER(s): N00014-79-0670
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, Purdue University, West Lafayette, IN 47907	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Department of the Navy, Arlington, VA 22217	12. REPORT DATE: April 1984
	13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

vibrational assignments, Raman and infrared spectra, SER spectra

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Detailed vibrational assignments are described for Surface Enhanced Raman (SER) spectra of pentaammineosmium(III), (II) and pentaammineruthenium(II) containing pyridine (py), pyrazine (pz), and 4,4'-bipyridine (bpy) ligands adsorbed at the silver-aqueous interface. The assignments are based on group symmetry analysis, deuteration effects, and by comparison with corresponding normal Raman and infrared spectra for the solid-phase complexes and surface and bulk Raman spectra for the corresponding free ligands. Most bands present in the normal Raman and/or infrared spectra also appear in the SER spectra. This

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results from the high intensity of the SER spectra along with the relaxation of vibrational selection rules for adsorbed molecules. The appearance of intense SER spectra for $Os(NH_3)_5py(III)/(II)$ and $Ru^{II}(NH_3)_5py$ is noteworthy since unlike free pyridine, these lack an available nitrogen for surface coordination. The results illustrate the virtues of electrochemical SER spectroscopy for examining the detailed vibrational properties of coordination compounds, including those in oxidation states (such as Os(II) here) that are difficult to obtain pure in bulk media.

SURFACE-ENHANCED RAMAN SPECTROSCOPY OF PENTAAMMINEOSMIUM(III)/(II) AND PENTAAMMINERUTHENIUM(II) CONTAINING PYRIDINE, PYRAZINE, OR 4,4'-BIPYRIDINE LIGANDS AT SILVER ELECTRODES: VIBRATIONAL ASSIGNMENTS

Stuart Farquharson, Peter A. Lay[‡], and Michael J. Weaver*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

ABSTRACT

Detailed vibrational assignments are described for Surface Enhanced Raman (SER) spectra of pentaammineosmium(III), (II) and pentaammineruthenium(II) containing pyridine (py), pyrazine (pz), and 4,4'-bipyridine (bpy) ligands adsorbed at the silver-aqueous interface. The assignments are based on group symmetry analysis, deuteration effects, and by comparison with corresponding normal Raman and infrared spectra for the solid-phase complexes and surface and bulk Raman spectra for the corresponding free ligands. Most bands present in the normal Raman and/or infrared spectra also appear in the SER spectra. This results from the high intensity of the SER spectra along with the relaxation of vibrational selection rules for adsorbed molecules. The appearance of intense SER spectra for $Os(NH_3)_5py(III)/(II)$ and $Ru^{II}(NH_3)_5py$ is noteworthy since unlike free pyridine, these lack an available nitrogen for surface coordination. The results illustrate the virtues of electrochemical SER spectroscopy for examining the detailed vibrational properties of coordination compounds, including those in oxidation states (such as Os(II) here) that are difficult to obtain pure in bulk media.

[‡]Department of Chemistry, Stanford University, Stanford, CA 94305.
Present address: Division of Applied Organic Chemistry, CSIRO, G.P.O. Box 4331, Melbourne, Victoria 3001, Australia

*Author to whom correspondence should be addressed.

INTRODUCTION

Although only in its infancy surface-enhanced Raman spectroscopy (SERS) has been demonstrated to be a valuable tool for gaining detailed structural information for molecules adsorbed at metal surfaces.[1] Preliminary investigations have demonstrated that a variety of adsorbates can be detected, from simple halide and pseudohalide anions[2,3] to complex molecules such as cytochrome c.[4] It also appears that the SERS effect may be limited to a select group of metal surfaces, most prominently silver, copper and gold.[1] Although a large proportion of SERS investigations have been aimed at elucidating the mechanism responsible for the unexpected signal enhancement, several practical applications are beginning to emerge. Thus SERS has yielded information on the nature of adsorbate-electrode bonding, and the alterations brought about by variations in electrode potential.[3,5] Also, recent studies indicate that under favorable conditions the Raman intensities are approximately proportional to adsorbate coverage.[6]

SERS studies are also starting to appear on adsorbates that undergo electrochemical reactions.[7-11] We have recently demonstrated that SERS can be utilized to follow heterogeneous electron transfer for several adsorbed redox couples,[8,9] including pentaammminepyridineosmium(III)/(II) and pentaammminepyrazineosmium(III)/(II), at the silver-aqueous interface.[8] These and related pentaammineosmium and pentaammineruthenium complexes containing nitrogen heterocycles are of particular interest since they form structurally simple transition-metal complexes that are substitutionally inert in both III and II metal oxidation states.[8] We have made quantitative comparisons of the potential-dependent SER spectra with the redox thermodynamics of these electroactive adsorbates obtained using conventional electrochemical techniques.[8b]

The present communication contains detailed vibrational analyses of SER spectra for $Os(NH_3)_5Py(III)/(II)$ [py = pyridine], $Os(NH_3)_5pz(III)/(II)$ [pz = pyrazine], $Os(NH_3)_5bpy(III)/(II)$ [bpy = 4,4'-bipyridine], $Ru^{II}(NH_3)_5py$, and $Ru^{II}(NH_3)_5pz$. Vibrational mode assignments are based on group symmetry considerations, combined with the frequency shifts observed upon selective deuteration, and comparison with corresponding bulk-phase normal Raman and Infrared spectra for these and related nitrogen heterocycle compounds. This report of the spectral details complements the comparisons of the potential-dependent spectral features with the electrochemical redox behavior of the complexes given in ref. 8b.

Although the silver electrode does perturb the vibrational properties of these adsorbates, the extent is small, especially for the pyridine adsorbates which lack an additional nitrogen for surface binding. The most detailed spectra data were gathered for $Os(NH_3)_5py(III)/(II)$ for which the most well-defined change in redox state from Os(III) to Os(II) is apparent upon altering the potential to more negative values.[8] Besides the remarkable intensity and richness of the SER spectra, some of these results demonstrate the virtue of the electrochemical SERS technique for obtaining detailed vibrational information for coordination compounds in very dilute solutions that are difficult or even impossible to observe by means of bulk-phase Raman or infrared measurements.

EXPERIMENTAL

The $Os^{III}(NH_3)_5py$, $Os^{III}(NH_3)_5pz$ and $Os^{III}(NH_3)_5bpy$ complexes were prepared as trifluoromethanesulfonate or halide salts as detailed in ref. 12a, and the corresponding Ru^{III} and Ru^{II} complexes as in ref. 12b. The SER spectra were obtained for 0.05 - 1 mM aqueous solutions of these complexes in either 0.1 M NaCl or NaBr. For the pyridine complexes, 0.1 M HCl was added in order to

suppress base-catalyzed disporportionation.[13] Other relevant details are given in ref. 8b.

The SERS electrochemical cell consisted of a cylindrical glass container with an optical flat base through which the laser beam was focussed on to the silver surface.[14] This electrode was of rotating disk construction, having an exposed face of diameter 0.4 cm, encased in a Teflon shroud. It was mechanically polished successively with 0.1μ and 0.3μ alumina immediately before immersion in the cell, and then electrochemically roughened in order to optimise the SERS intensities by means of an oxidation-reduction cycle (ORC) in the conventional manner.[1a,8b] The cell also contained an isolated silver-silver chloride or saturated calomel reference electrode, a platinum wire counter electrode, and an argon inlet tube for purging the solution.

Raman excitation was obtained using either a Spectra Physics Model 165 Kr^+ laser (647.1 nm) or Ar^+ laser (514.5 nm). The laser beam of 100 mW intensity was spot focussed at an incident angle of 60° to the electrode surface. The Raman scattering was collected at 90° to the surface, and focussed into a Jarrell-Ash Model 25/100 scanning double monochromator. The spectral resolution was ca. 4 cm^{-1}. The signal was detected with an RCA C31034 photomultiplier tube, amplified by a Victorean Model CTE-1 micro-microammeter, and displayed on a Hewlett-Packard Model 7100 strip chart recorder using a 1 cm sec^{-1} scanning rate and a 1 sec time constant. All spectra were frequency calibrated using laser plasma emission lines. Normal Raman and Fourier transform infrared spectra of the complexes were recorded as solid samples in KBr or CsI pellets. The former employed a rotating wheel to minimize photodecomposition. The latter were obtained using a Nicolet Model 7194 FTIR spectrometer.

Electrode potentials are quoted versus the saturated calomel electrode (sce). All experiments were conducted at 23 ± 1°C.

RESULTS AND DISCUSSION

Listings of the various surface-enhanced Raman (SER), normal Raman (NR), and infrared (IR) vibrational bands seen for each complex are given in Tables 1-5. SER spectra for the complexes are given for a representative pair of electrode potentials in order to provide a basic summary of the potential-induced spectral changes. For $Os(NH_3)_5py$, $Ru(NH_3)_5py$, and $Os(NH_3)_5pz$ (Table 1, 2, and 3, respectively) normal Raman and/or infrared data are given for both III and II metal oxidation states. For the first complex, the SER spectra obtained at -150 mV. vs sce are consistent with $Os^{III}(NH_3)_5py$ on the basis of frequency comparisons with the corresponding normal Raman spectrum, whereas that obtained at -750 mV corresponds to $Os^{II}(NH_3)_5py$.[8] On the other hand, the SER spectra for $Ru(NH_3)_5py$ and $Ru(NH_3)_5pz$ are consistent with the presence of Ru(II) throughout the observable potential region negative of ca -100 mV. at silver electrodes.[8] [The surface Os(III)/(II) formal potential, E_a^f, equals -670 mV.[8b]] Similarly, a number of potential-induced changes in the $Os(NH_3)_5pz$ SER spectra are consistent with reduction of Os(III) to Os(II) (E_a^f = -310 mV[8b]), although for this complex as well as for $Os(NH_3)_5bpy$ these changes do not appear to be associated simply with electroreduction of Os(III) to Os(II).[8b] (For simplicity the osmium and ruthenium oxidation states associated with particular vibrational modes will not be designated except where they are clear cut and/or the frequencies are sensitive to the oxidation state). For $Os^{III}(NH_3)_5py$ and $Os^{II}(NH_3)_5py$, SER frequencies are also given for samples where the pyridine ring or the ammine ligands were separately deuterated (Table 1).

Nearly all of the observed vibrational bands listed for these complexes in Table 1-5 can be accounted for in terms of metal-ligand, ammine, or nitrogen heterocycle modes. Included in these Tables along with the vibrational assignments are the associated symmetry species as well as a brief description. Following

standard nomenclature the stretching modes are designated ν, the in-plane bending modes δ, the out-of-plane bending modes γ, and the rocking modes ρ. The nitrogen heterocycle bands are additionally given Wilson mode numbers in accordance with established procedure.[15]

Metal-ligand modes.

The vibrational mode assignments are well established for transition-metal hexaammines[16] and for several pentaammine complexes.[17] For such pentaammine complexes with C_{4v} symmetry there are fifteen predicted metal-ligand vibrations; $4A_1$, $2B_1$, $1B_2$ and 4E symmetry species. (Note that only eleven unique modes result since the E modes are doubly degenerate.[18]) All of these modes are Raman active, whereas only the totally symmetric A_1 and the degenerate E modes are IR active. These modes are generally observed between 250 and 600 cm^{-1}.[17,19] In the present spectra as many as nine modes are observed in this spectral region. This compares favorably to the normal Raman spectra of metal halopentaammines which yield only four to seven observable peaks.[17] Similarly, at most three IR and two normal Raman peaks in this frequency region are observed for the present complexes (Tables 1-4). The absence of further peaks is presumably due to low signal intensities and accidental degeneracies. In addition to the modes given in Tables I-IV, the SER spectra also contain a low frequency band attributed to a silver surface-halide stretching mode from either the bromide or chloride ions used as the supporting electrolyte.[20] The presence of these anions is desirable for the production of stable intense SER spectra following the ORC.[8b] These surface-halide bands are easily identified by a frequency shift from around 240 to 180 cm^{-1} that occurs upon the substitution of bromide for chloride anions;[20] the SER spectra for the present complexes are otherwise unchanged.[8b]

The most interesting and indeed prominent band in the low frequency region of the SER spectra occurs around 300 cm^{-1}, and is attributed to a metal-nitrogen

heterocycle stretching mode, I (the metal-ligand modes are labelled with Roman numerals, see Tables 1-5). The unexpectedly high intensity of this mode may be attributable to interaction between the heterocycle with the electrode surface, via physical (or electrostatic) adsorption as in the case of the pyridine complexes and possibly via chemisorption of the remote nitrogen for the pyrazine and bipyridine complexes. Indeed, the greater surface-heterocycle interaction expected with the latter adsorbates may well be related to the particular intensity of this and the other SERS bands with these systems.[8b]

The band at 267 cm^{-1} seen for $Os(NH_3)_5py$ at -750 mV is ascribed to Os(II)-pyridine stretching. Although a very weak band at 291 cm^{-1} appearing at less negative potentials was originally ascribed to an Os(III)-pyridine vibration,[8a] this assignment is probably incorrect.[8b] For the pyrazine complexes, mode I is tentatively assigned to the band that occurs between 300 and 350 cm^{-1} (Tables 3 and 4). The appearance of a band at 304 cm^{-1} at more negative potentials for $Os(NH_3)_5pz$ may be associated with the Os(II) complex. However, these potential-dependent changes do not appear to be associated with a simple adsorbed redox couple since the higher frequency band (345 cm^{-1}) persists even at negative potentials (Table 3).[8b] A puzzling feature is the surprisingly high frequencies at which these bands appear for the pyrazine complexes: metal-pyrazine stretching modes are typically observed for divalent pyrazine complexes at ca. 250-280 cm^{-1}.[22] The present higher frequencies may arise from surface binding of the pyrazine ligand. Peaks around 300-330 cm^{-1}, ascribed to metal-pyrazine stretching, can also be seen for binuclear metal complexes containing pentaammminepyrazineruthenium(II).[23,24] The strong SER bands seen at 370-400 cm^{-1} for $Os(NH_3)_5bpy$ (Table V) are also somewhat puzzling in this regard. However, intense modes at similar frequencies have also been observed for Ru^{II}(2,2'-bipyridine)$(py)_4$ both at silver electrodes and in bulk media.[25]

The metal-ammine modes are expected to shift to lower frequencies by a factor of 0.92 upon deuteration of the ammine modes on the basis of the square root of the ligand mass ratio $(17/20)^{\frac{1}{2}}$. Such deuteration effects were examined for SERS of $Os(NH_3)_5py(III)/(II)$ for which the most well-defined metal-ammine modes were observed (Table 1). Precisely such a shift occurs for the $Os^{III}(NH_3)_5py$ band at 494 cm^{-1} and the $Os^{II}(NH_3)_5py$ band at 468 cm^{-1}. Although these bands also exhibit small decreases upon deuteration of the pyridine ligand (Table 1), these shifts can be rationalized in terms of coupling between the metal-ammine and metal-pyridine modes. Such coupling is anticipated for E symmetry metal-ammine modes.[17]

The band around 415 cm^{-1} for $Os(NH_3)_5py$ is most likely due to a pyridine ring mode (vide infra). Although several other SERS bands occur in the frequency region 400-550 cm^{-1} for the various complexes which are probably due to other metal-ammine modes, unambiguous assignments are lacking in some cases (Tables 1-5). A difficulty with the pyrazine complexes is that most metal-ligand modes are dwarfed by the intensity and breadth of the metal-pyrazine modes noted above. Several of these modes are nonetheless observed in the IR and Raman spectra and are assigned according to their expected activity from selection rules (Tables 3 and 4).

Internal Ammine Modes

All five internal ammine vibrational modes expected are commonly observed as strong bands in the IR spectra for metal ammine complexes.[16,19] Of these, SERS bands at 3200, 1620, and 1350 cm^{-1} are observed for $Os^{III}(NH_3)_5py$ which can be ascribed to N-H stretching, and asymmetric and symmetric NH_3 bending, respectively (Table 1). The last-named mode is of particular interest as its frequency decreases about 100 cm^{-1}, from 1354 to 1254 cm^{-1}, upon reduction of Os(III) to Os(II) (Table 1). Such a strong sensitivity of this band to the nature of the coordinated metal, including the metal oxidation state, has been noted

previously.[16] This assignment is also supported by the large deuterium isotope effect observed for this mode (Table 1). The assignment for the 1620 cm^{-1} band is also supported by the substantial frequency decrease seen upon deuterium isotope substitution (Table 1). However, the band at 3200 cm^{-1} appears to be complicated by accidental degeneracy with the C-H stretching modes also expected in this region (Table 1). Several of these modes also appear in the SER spectra for the other complexes, although they are probably obscured in some cases by the more intense heterocycle ring modes. The ammine rocking mode is observed in the SER spectra for $Ru(NH_3)_5py$, nearly coincident in frequency to its IR value of 815 cm^{-1} (Table 2).

It should be noted that the appearance of metal-ammine and internal ammine modes in the SER spectra is in itself noteworthy since the ammine ligands are not expected to interact with, and may well be relatively remote from, the metal surface. Nevertheless, we have recently demonstrated that intense SER spectra are obtained even for transition-metal *hexaammine* complexes that are electrostatically adsorbed at silver electrodes in halide media.[9] Bands associated with both metal-ammine and internal ammine modes are observed.[9] These conditions are similar to those employed here and indeed suggest that both adsorption and the consequent appearance of SER spectra of the nitrogen heterocycle complexes may be associated as much with strong electrostatic attraction of the multicharged cationic complexes to the specifically adsorbed halide anions as with surface binding of the heterocyclic ligands.[8b]

Internal Pyridine Modes

Nearly all the remaining SER vibrational bands can be accounted for in terms of internal nitrogen heterocycle modes. The SERS vibrational mode assignments for the present pyridine and pyrazine complexes are aided considerably by the availability of detailed SERS studies of the adsorbed free ligands at silver electrodes.[26,27] Summaries of representative SER spectra for free pyridine and pyrazine obtained in the present work are also given in Tables 2 and 4, respectively. A further aid to spectral assignments was provided by the influence of pyridine ring deuteration upon the SERS vibrational frequencies for $Os(NH_3)_5py$ (Table 1).

The 27 vibrational modes expected for pyridine, assuming C_{2v} symmetry, consist of $10A_1$, $3A_2$, $9B_1$, and $5B_2$ symmetry modes.[15,27] All these modes are expected to be both Raman and IR active. Although there are three fewer vibrational modes predicted for pyridine than benzene, (those absent have Wilson mode numbers 7a, 9b, and 17b[15]), the lower molecular symmetry for pyridine lifts the degeneracy of the remaining modes, yielding more spectral peaks. Most of these modes are observed in the SER spectra of adsorbed pyridine; and as expected, bands arising from the A_1 modes are the most intense.[27] The frequencies are very close to those for bulk-phase aqueous pyridine.[26,27] Bands corresponding to most of these modes are also seen in the SER spectra of $Os(NH_3)_5py$ and $Ru(NH_3)_5py$ (Tables 1 and 2). For free pyridine at silver the most prominent SERS bands occur at ca. 1007, 1035, 1216, and 1597 cm^{-1}, corresponding to the totally symmetric ring breathing mode (Wilson mode 1), the trigonal ring breathing mode (12), a symmetric in-plane C-H bending mode (9a), and another ring breathing mode (8a; Table 2). For SERS of $Os^{III}(NH_3)_5py$, these modes are observed at 1020, 1076, 1216, and 1592 cm^{-1} (Table 1). It is interesting to note that similar frequencies are seen for these modes in the

bulk-phase IR and normal Raman spectra, although the latter spectrum is relatively sparse.

Electroreduction of adsorbed $Os^{III}(NH_3)_5py$ to $Os^{II}(NH_3)_5py$ yields noticeable frequency decreases of the 1020 cm^{-1} band to 992 cm^{-1} and the 1076 cm^{-1} band to 1054 cm^{-1}, whereas the other two modes noted above remain relatively unaltered (Table 1). These frequency shifts can be understood in terms of the additional electron density expected on the pyridine ring when coordinated to Os(II) rather than Os(III).[8] For $Ru^{II}(NH_3)_5py$, these four SERS bands occur at 1011, 1054, 1222, and 1591 cm^{-1} (Table 2). The higher frequency of the first mode for Ru(II) relative to that for Os(II) is compatible with the smaller extent of metal-pyridine back bonding expected for the former complex.[8b] Additional A_1 modes are observed in the SER spectra for these complexes at ca. 650 (6a), 1050 (18a), 2900 (13), and 3200 cm^{-1} (2). The opposite assignments are usually given for modes 12 and 18a. The present assignment is made, albeit tentatively, on the expectation that the more symmetrical trigonal ring breathing mode 12 will have a larger intensity as well as a greater sensitivity to the metal oxidation state.

Deuteration of the pyridine ring on $Os^{III}(NH_3)_5py$ and $Os^{II}(NH_3)_5py$ shifts the 6a, 1, 12, 18a, and 8a modes to lower frequencies by factors close to the ratio 0.97 observed for bulk-phase pyridine and metal pyridine complexes (Table 1);[28] such shifts are consistent with the assignment of these bands to ring modes.[28] The corresponding deuteration frequency ratios for the 12, 9a, and 13 modes were around 0.73, as expected for C-H modes, and again consistent with the effects of deuteration upon bulk-phase pyridine spectra.[28]

Although pyridine deuteration shifts Wilson mode 2 for $Os^{III}(NH_3)_5py$ to around 2300 cm^{-1}, a smaller peak remains at 3200 cm^{-1} (Table 1). This is

most likely due to the N-H stretching mode appearing upon removal of the accidental degeneracy of these two modes (vide supra). The breadth of the latter adds to the difficulty in making distinct assignments in this frequency region. Thus although the 20a mode is also anticipated in this region, it is not observed and may be buried beneath stronger peaks. The assignment of the 2900 and 3200 cm^{-1} bands to modes 2 and 13 is based on their expected greater intensity.[27]

Of the three predicted A_2 modes (10a, 16a, 17a), only the first is detected in the SER spectra, appearing for $Ru^{II}(NH_3)_5py$ at ca. 735 cm^{-1} (Table 2). Most of the nine B_1 modes can be accounted for in the present spectra. Peaks at ca. 1150, 1450 and 1575 cm^{-1} for pyridine on silver (Table 2) are similarly observed for the pyridine complexes and thus are assigned 9b, 19b and 8b, respectively. The 1150 cm^{-1} band for $Os(NH_3)_5py$ could alternatively be assigned to mode 15. The absence of the pyridine mode 6b for SERS of $Os(NH_3)_5py$ and $Ru(NH_3)_5py$ (Tables 1,2) may be due to accidental degeneracy with mode 6a. Since a large change in dipole moment and reduced symmetry will favor the appearance of modes 3, 7b and 20b to a greater extent in the IR than the NR spectra, it is not too surprising that they are not detected in the SER spectra. Their appearance in the IR spectra at ca. 1245, 2950, and 2980 cm^{-1} support these assignments. Mode 14 occurs in both the IR and SER spectra of $Os(NH_3)_5py$ at 1385 cm^{-1} and shifts as expected[28] to ca. 1320 cm^{-1} upon deuteration (Table 1).

The remaining $5B_2$ modes are all out-of-plane vibrations and are observed below 1000 cm^{-1} in the SER spectra of $Os(NH_3)_5py$. Some of these modes can be identified by comparison with the pyridine SER spectra. Thus the 415 cm^{-1} band for $Os(NH_3)_5py$ (Table 1) is close to the frequency expected for the pyridine ring mode 16b.[27] Indeed pyridine deuteration decreases the frequency

by the factor 0.92, in good agreement with that seen for pyridine and other pyridine complexes.[28] Further support to this assignment over the alternative designation as a metal-ammine vibration (vide supra) is given by the observed insensitivity of the frequency to the osmium oxidation state (Table 1). Assignment of the band around 900 cm^{-1} for $Os(NH_3)_5py$ to the C-H stretch mode 10b is similarily supported by the frequency decrease by the factor 0.78 seen upon pyridine deuteration (Table 1). Modes 10a, 11 and 4 are expected to occur around 700 cm^{-1}.[15] The latter two modes are expected to yield strong IR bands on the basis of their B_2 symmetry; they are thereby assigned to the bands at ca. 740 and 760 cm^{-1}, respectively for $Os(NH_3)_5py$ (Table 1).

In addition, several unassigned peaks are observed in the SER spectra, most notably at 1271 cm^{-1} for $Os(NH_3)_5py$, and 518 cm^{-1} and 1176 cm^{-1} for $Ru^{II}(NH_3)_5py$. These peaks may be due to combinations, overtones, Fermi resonance, or to adsorbed impurities.

Several general trends are apparent when viewing Tables 1 and 2. In particular, complexation of pyridine to osmium or ruthenium shifts several modes by 10-20 cm^{-1} to higher frequencies. A similar observation has also been made for other metal pyridine complexes, and attributed to coupling of the pyridine ring modes with the metal-ligand vibrations.[21a] As noted above, similarly to the metal-ammine modes several of the pyridine modes shift significantly upon alteration of the metal oxidation state. However, it also should be noted that the frequencies of the SER spectra are not significantly shifted (<5 cm^{-1}) compared to the corresponding IR and normal Raman values for the complexes. This is indicative of only weak interactions between the adsorbed complexes and the silver surface.

Internal Pyrazine Modes

There are 24 predicted vibrational modes for pyrazine, consisting of $5A_g$, $1B_{1g}$, $4B_{2g}$, and $2B_{3g}$ Raman-allowed modes, $2A_u$ forbidden modes, and $4B_{1u}$, $2B_{2u}$, and $4B_{3u}$ infrared-allowed modes for D_{2h} symmetry (g: gerade; u: ungerade). Thus there are five fewer modes expected for pyrazine than pyridine; these are the two A_u modes (16a and 17a), one B_{3g} mode (10b), one B_{3u} mode (18b), and one B_{1u} mode (20a). Although the symmetrical nature of pyrazine makes the appearance of Raman and IR modes mutually exclusive, adsorption as well as metal coordination will relax this rule somewhat.[31] Furthermore, the greater adsorbate-surface interactions expected to result from surface attachment of the remote pyrazine nitrogen may well shift the band frequencies and alter their relative intensities, making the assignments somewhat more tentative.

Again the most prominent modes in the normal Raman and SER spectra for $Os(NH_3)_5pz$ and $Ru(NH_3)_5pz$, as well as the SER spectra of free pyrazine, are the totally symmetric modes (A_g; Tables 3 and 4). The observed frequencies at ca. 1020, 1230, and 1600 cm^{-1} for these complexes are assigned to modes 1, 9a and 8a, as deduced from the similar frequencies found for liquid pyrazine,[15] pyrazine adsorbed at silver,[27] and bulk-phase metal pyrazine complexes.[30] The appearance of these modes for the complexes with considerable intensity in the IR spectra is indicative of selection rule breakdown.

The other two A_g mode assignments are not so clearcut. Several peaks appear between 600 and 750 cm^{-1}, where the 6a mode is expected along with modes 6b (B_{2g}) and 4 (B_{3g}). The lower two frequency peaks have been alternately assigned to modes 6a and 6b, while mode 4 is generally assigned to the highest frequency.[15,27,31,32] Of these the most intense peak in the Raman spectra for

$Os(NH_3)_5pz$ and $Ru(NH_3)_5pz$ occurs at ca. 700 cm^{-1} and is therefore assigned to the A_g mode 6a. Modes 6b and 4 are then assigned to the 660-680 cm^{-1} and ca. 735 cm^{-1} peaks, respectively.

The final A_g mode (2) is left unassigned; N-H stretching modes occur in the ca. 3100 cm^{-1} frequency region, where this band is expected (vide supra) (Table 3 and 4). Although a C-H stretching mode is observed for $Ru(NH_3)_5pz$ at 3010 cm^{-1} its frequency corresponds most closely to mode 7b (B_{2g}) for pyrazine at silver[27]. Two other C-H stretching modes are seen for these complexes, but only in the IR spectra. They are assigned to the ungerade symmetry modes 13 (B_{1u}) and 20b (B_{3u}), on the basis of data for similar metal-pyrazine complexes.[30]

Of the B_{1u} modes, only the trigonal ring breathing mode 12 is clearly detected in the SER spectra for $Os^{III}(NH_3)_5pz$ and $Ru^{II}(NH_3)_5pz$. Although mode 18a is expected at similar frequencies it may be hidden by the more intense mode 12. The remaining B_{1u} modes 13 and 19a are observed in the IR spectra as expected (Tables 3 and 4).

For the remaining symmetry species only a few modes [4 (vide supra), 10a, 11, 14 and 19b] show detectable SER bands. These modes were again assigned chiefly by comparison with previous analyses for bulk-phase and adsorbed pyrazine.[27] A number of additional bands are found in the IR spectra and are assigned based on symmetry arguments and comparison with literature assignments.[30] Several peaks at ca. 520, 1040 (Raman and IR only) and 1420 cm^{-1} for $Os(NH_3)_5pz$ and ca. 520, 1030, 1260 and 1420 cm^{-1} for $Ru(NH_3)_5pz$ remain unassigned, and again may be attributed to overtones, combinations or Fermi resonance.

Similar to the pyridine complexes, $Os(NH_3)_5pz$ and $Ru(NH_3)_5pz$ exhibit several bands having potential-dependent frequencies, in particular metal-ligand

mode I and pyrazine modes 1, 6a, and 12. However, as mentioned above these shifts are not wholly associated with an oxidation state change for the coordinating metals, especially since the formal potential for the Ru (III/II) couple is positive of the potential region studied.[8b] These potential dependencies appear to be due in part to the involvement of different surface sites, molecular orientations, etc., possibly associated with specific interactions of the pyrazine ligand with the silver surface.[8b]

Internal Bipyridine Modes

The $Os(NH_3)_5bpy$ SER spectra are necessarily more complicated, due to the increased number of vibrational modes. The measurements were limited to a relatively cursory study of the SERS of $Os(NH_3)_5bpy$ and bipyridine (Table 5). However, reasonable assignments can be ascertained if a flat molecule is assumed, i.e. the rings are contained in the same plane. The molecule then has D_{2h} symmetry with 54 predicted vibrations. Group symmetry arguments yield 10Ag $3B_{1g}$, $9B_{2g}$ and $5B_{3g}$ Raman active modes, 4Au forbidden modes and $9B_{1u}$, $5B_{2u}$ and $9B_{3u}$ infrared active modes. Most of the observed modes can be assigned primarily by comparison with previous vibrational analyses of related molecules, especially biphenyl.[33]

In group symmetry analyses the choice of axis labels is somewhat arbitrary. The x, y and z axis were chosen in the present study to be consistent with the above analysis of pyridine and pyrazine. The axis have therefore been interchanged with those employed for biphenyl such that the Wilson numbering scheme can be maintained.[33] Each pyridine mode is split into an in-phase and out-of-phase component for the bipyridine complex. Thus the pyridine A_1 modes become an A_g mode where the two ring motions are in-phase and a B_{1u} mode were the ring motions are out-of-phase. By analogy to biphenyl, the former modes are shifted to higher frequencies, whereas the latter

modes are unaffected and are comparable in frequency to the corresponding pyridine modes. Although extensive normal coordinate analysis has been carried out for only the in-plane biphenyl modes,[33] these constitute the majority of the experimentally observed modes. These include the A_g, B_{1u}, B_{2g} and B_{3u} modes.

Similarly to pyridine and pyrazine ligands, the most intense SERS bands for $Os(NH_3)_5$bpy and bipyridine were found to be the symmetric in-phase stretching modes (A_g) (Table 5). The remaining A_g modes 2 and 13 occur in the high frequency region, but unfortunately these peaks were broad and weak and therefore are not reported in Table 5. The out-of-plane compliments to the A_g modes, the B_{1u} modes, also have significant intensity in the SER spectra. These modes are easily assigned by their nearly coincident frequencies with those for pyridine. Of the remaining eighteen in-plane modes only four (6b, 8b, 15, 18a) are observed for bipyridine and two (6b, 8b) for $Os(NH_3)_5$bpy (Table 5). Since the in- and out-of-plane component of these modes are predicted to occur at approximately the same frequency and only one spectral peak appears, no phase assignment is made for modes 15 and 8b. Several out-of-plane modes also appear but are generally weak. Other bands due to out-of-plane modes are also anticipated to be relatively weak. Since they are expected to occur at similar frequencies to the in-plane modes, they may not be observed due to accidental degeneracy.

Additionally, two new modes occur in the spectra due to inter-ring stretching. Both are of A_g symmetry and are found at ca. 355 and 1295 cm^{-1} for bipyridine and ca. 1305 cm^{-1} for $Os(NH_3)_5$bpy. For the latter adsorbate the lower frequency mode may be hidden by the intense metal-ligand mode I (Table 5).

Viewing Table 5 reveals several general features. It is noticably devoid of metal-ammine and other metal-ligand modes. This may be due to a reduced SER enhancement caused by the greater distance between the metal center and the electrode surface. The totally symmetric pyridine modes (A_1) are nearly all observed as pairs composed of in- and out-of-phase components although, the former modes are generally more intense. By analogy with the potential-dependent $Os(NH_3)_5py$ and $Os(NH_3)_5pz$ spectra, the appearance of the band at 996 cm^{-1} for $Os(NH_3)_5bpy$ as the potential is made more negative may be associated with the formation of the Os(II) oxidation state, as is the appearance of a lower frequency metal-ligand stretching mode under these conditions. Indeed, such a redox state change is consistent with the electrochemical data.[8b] However, as for $Os(NH_3)_5pz$ the higher frequency band also survives at more negative potentials, suggesting that more than one type of adsorbate stereochemistry may be involved. However, the additional structural complexity of the bipyridine adsorbates render such interpretations somewhat speculative.

CONCLUSIONS

The intensity and richness of the present SER spectra, coupled with the need to employ only very small quantities of material, suggest that the technique may have wide utility for obtaining detailed vibrational information for coordination compounds that can be chemically or electrostatically adsorbed at metal surfaces. Indeed the signal intensities are commonly as great as those obtained for resonance Raman spectroscopy. Although the relaxation of selection rules for SERS yields more complete vibrational spectra, this makes the assignment of vibrational modes necessarily more complicated. Nevertheless, this can be minimized by careful comparisons with bulk NR and IR spectra. An additional important virtue of the SERS method is that it enables spectra to be obtained for species, such as Os(II), that are difficult to examine in

bulk media due to their chemical instability. Further applications of SERS for examining the molecular structural details of electrochemical redox processes involving coordination compounds at silver and gold electrodes are being pursued in this laboratory.

ACKNOWLEDGMENTS

PAL acknowledges a CSIRO postdoctoral fellowship, and MJW a fellowship from the Alfred P. Sloan Foundation. This work is supported in part by the Office of Naval Research and the Air Force Office of Scientific Research.

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Table 1. Summary of SER spectra for $Os(NH_3)_5pv(III),(II)$; effects of pyridine ring and ammine deuteration, and comparison with normal Raman and infrared spectra.

Mode Number[a]	Symmetry Species[b]	Brief Vibrational Description[c]	IR[e,i,h]	IR[e,h]	Raman[e,f]	SERS					
								pyridine-D_5[e]		ND_3[m]	
			Os(III)	Os(II)	Os(III)	-150 mV	-750 mV	-150 mV	-750 mV	-150 mV	-750 mV
I	A_1	$\nu_{M-N'}$					267s		263m		256s
16b	B_2	γ_{ring}				415w	417w	381m	384w		
		u	444m								
VIII	E	ν_{M-N_2}	466m								
XI	E	$\nu_{M-N_3N'}$				494w	468m	480m	460m,br	461m	436m
II	A_1	ν_{M-N_4}			501w						
		u	520s								
III	A_1	ν_{M-N}				573w,br	557m,br				
6a	A_1	δ_{ring}	649w		654m	654m	648s	623w	618m	655m	647m
11	B_2	γ_{C-H}	696vs		704m		739w			701m	698w
4	B_2	γ_{C-H}	760vs				765w				
10a	A_1	γ_{C-H}	790m				807w				
	E	ρ_{NH_3}(rock)	851vs,br								
10b	B_2	γ_{C-H}				895w	900m		702m		898w
5	B_2	γ_{ring}	955w				960w		797w		
1	A_1	ν_{ring}	1022m	990m	1020s	1020vs	992s	978vs	955s	1019vs	989s
18a	A_1	δ_{C-H}	1055vw			1050w		1022w			
12	A_1	ν_{ring}	1074s	1055w		1076m	1054s	1042m,sh	1025m	1078m	1054m
9b/15	B_1	δ_{C-H}	1157m		1154vw	1151w	1151w				
9a	A_1	δ_{C-H}	1216m,br		1221m	1216m,br	1210s		896m	1220s	1210s
3	B_1	δ_{C-H}	1241w								
		u	1269w			1271m		1234m		1267w	
	E	δ_{NH_3}(sv)	1347vs			1354m	1254w,sh			1085m,sh	
14	B_1	δ_{C-H}	1373s,sh			1386s	1385w	1322vs	1325m	1321s	
19b	B_1	ν_{ring}	1442vs			1441w	1430w,br			1443w	
19a	A_1	ν_{ring}	1494s								
8b	B_1	δ_{C-H}	1584s,sh								
8a	A_1	δ_{C-H}			1600m,sh	1592vs,br	1593s	1552vs	1550s	1607vs,br	1593vs
	E	δ_{NH_3}(as)	1608vs		1613s	1620s,br		1604vs	1600m,br	1170s	
13	A_1	ν_{C-H}				2900w,br	2910w,br		2100m,br		
7b	B_1	ν_{C-H}	2940m							2930s	2920m,br
2	A_1	ν_{C-H}				3200m,br	3210m,br	2310m			
	A_1	ν_{NH_3}	3150vs,br			3200m,br	3210m,br	3220s,br	3230s,br		

...ab,c ... infrared spectra of $Ru(NH_3)_5$pyridine(III), (II), and ... of pyridine.

Mode Number[a]	Symmetry Species[a]	Brief Vibrational Description[b]	$Ru(NH_3)_5$py						pyridine[k]	
			IR[c,g]		Raman[e,g]		SERS		SERS	
			Ru(III)	Ru(II)	Ru(III)	Ru(II)	-150 mV	-450 mV	-150 mV	-650 mV
I	A_1	$\nu_{M-N'}$					303vs	297s		
16b	B_2	γ_{ring}	413vw				419vw,br	416vw	412vw	
VIII	E	ν_{M-N_2}	464s	456w	465m			456vw		
XI	E	$\nu_{M-N_3N'}$	482m,sh	470w						
11	A_1	ν_{M-N_4}	496m,sh	498w	494m					
							518m	517w		
6a	A_1	δ_{ring}	648m	640w	646m	646m	654vs	655s	625w	627w
6b	B_1	δ_{ring}							651vw	654w
11	B_2	γ_{C-H}	703vs	693m			683s	682m		
10a	A_1	γ_{C-H}					736m	734w		
4	B_2	γ_{C-H}	777vs	770m					755w,br	757w,br
	E	$\rho_r NH_3$(rock)	825vs,br	815s,br			816m	817m		
10b	B_2	γ_{C-H}	894w						880vw,br	875vw,br
5	B_2	γ_{ring}					959w,br		943vw	943vw
1	A_1	ν_{ring}	1017s	998s	1023s	1011s	1011s	1012s	1007vs	1006s
12	A_1	ν_{ring}	1069s	1050m		1057w	1054s	1054s	1037s	1034s
18a	A_1	δ_{C-H}	1050w						1067w	1065s
15	B_1	δ_{C-H}	1153m,sh	1150w				1144vw	1154vw	1153vw
9b	B_1	δ_{C-H}	1176s	1176m						
9a	A_1	δ_{C-H}	1223m		1218s	1217s	1222vs	1222s	1216m	1216m
3	B_1	δ_{C-H}	1245m							
			1292s							
	E	δ_{NH_3}(sy)	1325vs				1260m			
			1356s	1328m			1360m,br	1368vw,br		
14	B_1	δ_{C-H}	1393s	1390m						
19b	B_1	ν_{ring}	1446vs	1446s			1468m	1468m	1445vw	
19a	A_1	ν_{ring}	1493vs	1490m					1487vw	1482vw
8b	B_1	δ_{C-H}							1573w	1573w,sh
8a	A_1	δ_{C-H}		1605s	1606s	1601s	1591vs	1591s	1597m	1597s
	E	δ_{NH_3}(as)	1609vs	1610s,br		1611vw				
7b	B_1	ν_{C-H}	2951s,sh	2940s,sh						
20b	B_2	ν_{C-H}	2981s,sh	2980w						
2	A_1	ν_{C-H}							3060s,br	3050s,br
	E	$\nu_{N-H(sy)}$	3140vs,br	3115m,sh						
	A_1	$\nu_{N-H(as)}$		3200s,br						

Table 3. Summary of SER, Raman, and infrared spectra for $Os(NH_3)_5pz(III,(II)$; effect of amine deuteration.

Mode Number[a]	Symmetry Species[b]	Brief Vibrational Description	IR[d]	IR[b]	Raman[f]		SERS			
									ND_3[m]	
			Os(III)	Os(II)	Os(III)	Os(II)	-150 mV	-550 mV	-150 mV	-550 mV
I	A_1	$\nu_{M-N'}$			350vw	287s	345vs	304vs 343s	345vs	299vs 340s
VIII	E	ν_{M-N_2}		450m			461w	440vw		
16b	B_{2u}	γ_{ring}					494w	496w	487w	487w
		u	524m	515m						
III	A_1	ν_{M-N}	557m							
6b	B_{2g}	δ_{ring}	684m		658m	662m				
6a	A_g	δ_{ring}		700s	710s	707s	702s	673vs 699m	701s	670vs 700m
4	B_{3g}	γ_{C-H}					736m	736w		739w
10a	B_{1g}	γ_{C-H}		771m				762w		
11	B_{2u}	γ_{ring}	816w,sh				820vw	814w	816w	807m
	E	ρ_{NH_3}(rock)	848s	810s						
5	B_{3g}	γ_{ring}	874s							
1	A_g	ν_{ring}	1022m	1000s	1021m	988m	1020s	985m 1020m	1019s	991m 1020m
		u	1040m	1034s		1045w				
12	B_{1u}	ν_{ring}	1091m	1067s		1070m	1069m 1095s	1067vs 1088m,sh	1070m,sh 1089s	1066vs 1087m,sh
15	B_{3u}	δ_{C-H}	1157s	1162s						
9a	A_g	δ_{C-H}	1251m	1232m	1236m	1240m	1232s	1223m	1230s	1224s
	E	δ_{NH_3}(sy)	1339m,sh 1355s	1263vs						
14	B_{3u}	δ_{C-H}		1358w			1365vw	1366m		1318vw
		u	1425m	1415m	1416vw	1417vw	1418vw	1433w		
19b	B_{3u}	ν_{ring}	1441m	1445s			1464m	1464s	1464s	1464s
19a	B_{1u}	ν_{ring}	1497w	1490m						
8b	B_{2g}	δ_{C-H}	1592s,sh	1586m,sh						
8a	A_g	δ_{C-H}		1608s,sh	1603m	1601s	1602s	1590m	1600s	1594s
	E	δ_{NH_3}(as)	1606s,br	1616s	1614w					
20b	B_{3u}	ν_{C-H}	2978m	2979m						2925m
7b	B_{2g}	ν_{C-H}	3022s							
13	B_{1u}	ν_{C-H}	3075s							
	A_1	$\nu_{N-H(sy)}$		3119s,sh						
	A_1	$\nu_{N-H(as)}$	3220s,br	3201s,br			3230w,br	3220m,br		

Table 4. Summary of SER, Raman, and infrared spectra for $Ru(NH_3)_5pz(II)$; comparison with SER spectra for pyrazine.

Mode Number[a]	Symmetry Species[b]	Brief Vibrational Description[c]	$Ru(NH_3)_5pz$				pyrazine[k]	
			IR[e,i]	Raman[e,i]	SERS		SERS	
			Ru(II)	Ru(II)	-50 mV	-650 mV	-150 mV	-650 mV
I	A_1	$\nu_{M-N'}$		327vw	325s,br	302s,br		
16a	A_u	γ_{ring}	377w					354w
VIII	E	ν_{M-N_2}	456w	451vw	455vw			
XI	E	$\nu_{M-N_1N'}$	472w					
16b	B_{2u}	γ_{ring}	504w				441m	434m
		u			524m	522m		
III	A_1	ν_{M-N}		556w	568w			
6a	A_g	δ_{ring}		692m	687s	675s	639s	636s
6b	B_{2g}	δ_{ring}	640s			642m	674m,sh	660m,sh
*	B_{3g}	γ_{C-H}			736m	735m	699m	699m
10a	B_{1g}	γ_{C-H}	753sh,br				742m	744m
	L	$\rho_{NH_3(rock)}$	780s					
11	B_{2u}	γ_{C-H}			820m	819m	806m	812m,br
	B_{3g}	γ_{ring}					898vw	
1	A_g	ν_{ring}	1013m	1019m	1019s	1016s	1020s	1021s
		u	1030w				1050w	
12	B_{1u}	ν_{ring}		1076m,br	1077s	1056m,sh 1074m	1088m	
18a	B_{1u}	δ_{C-H}					1061w	1064w
3	B_{2g}	δ_{C-H}	1107w		1102w,sh	1101m,sh	1124w	1110w
15	B_{3u}	δ_{C-H}	1153w		1152w	1149vw	1160vw	1160vw
9b	B_{2u}	δ_{C-H}	1170w		1190w	1190vw		
9a	A_g	δ_{C-H}	1221s	1229s	1227vs	1223s	1225s	1225s
		u			1268m	1260m	1246m,sh	
	L	$\delta_{NH_3(sy)}$	1295s 1316s 1348s		1339w			
14	B_{3u}	δ_{C-H}	1386w		1383w		1361w,br	1360w,br
		u	1420s		1426w	1419w		
19b	B_{3u}	ν_{ring}	1467m		1472m	1471m	1464w	1467w
19a	B_{1u}	ν_{ring}	1480m				1479w	1479w
8b	B_{2g}	δ_{C-H}			1565m,sh	1563m,sh	1519m	1521m
8a	A_g	δ_{C-H}	1579s	1601s	1593vs	1591s	1590vs	1588vs
	L	$\delta_{NH_3(as)}$	1620s,br					
20b	B_{1u}	ν_{C-H}	2961m,br					
7b	B_{3g}	ν_{C-H}				3010w,br		3030w,br
13	B_{3u}	ν_{C-H}						3050w,br
	A_1	$\nu_{N-H(as)}$	3140s,br					
2	A_g	ν_{C-H}						3175w,br
	A_1	$\nu_{N-H(sy)}$	3282s,br					

Table 5. Summary of SER spectra for $Os(NH_3)_5bpy(III),(II)$ and 4,4'-bipyridine.

Mode Number[a]	Symmetry Species[b]	Phase[d]	Brief Vibrational Description[c]	$Os(NH_3)_5bpy$ SERS -150 mV	$Os(NH_3)_5bpy$ SERS -850 mV	bipyridine[k] SERS -150 mV	bipyridine[k] SERS -650 mV
	A_g		ν_{r-r}				355vw
I	A_g		$\nu_{M-N'}$	388vs,br	368m 397s		
16a	A_u	i	γ_{ring}			390m	386m
16b	B_{2u}	i	γ_{ring}				497vw
		u				530m	
6a	B_{1u}	o	δ_{ring}	636vs	637m		625m
6b	B_{2g}	i	δ_{ring}	655w	651m	674w	666w
6a	A_g	i	δ_{ring}	770s	769s	767m	771s
11	B_{2u}	o	γ_{C-H}				806vw
10b	B_{3g}	o	γ_{C-H}				866w
5	B_{3g}	o	γ_{ring}			938m	942w
1	B_{1u}	o	ν_{ring}		996s	1004vs	
1	A_g	i	ν_{ring}	1005vs	1010s		1014vs
		u		1021m,sh	1024w,sh		
12	B_{1u}	o	ν_{ring}				1045w
12	A_g	i	ν_{ring}	1057vs	1053s	1058m	
18a	B_{3u}	i	δ_{C-H}				1078m
15	B_{3u}	i	δ_{C-H}			1141vw	1140m
9a	B_{1u}	o	δ_{C-H}	1209vs	1210m,sh	1197m,sh	
9a	A_g	i	δ_{C-H}	1228s,sh	1224s	1218s,br	1224s,br
	A_g		ν_{r-r}	1305s	1301m,br	1296s	1295vs
		u				1334s	
19a	B_{1u}	o	ν_{ring}	1481m	1475m		
19a	A_g	i	ν_{ring}	1520s	1511m,br	1507s,sh	1516s
8b			δ_{C-H}	1580s	1587vs	1558vs	
8a	B_{1u}	o	δ_{C-H}	1603vs	1604s	1593vs	1606vs
8a	A_g	i	δ_{C-H}	1628vs	1628s,sh	1634vs	1630s,sh

Footnotes to Tables 1-5.

Frequencies listed are typically accurate to within 2-3 cm^{-1}.
Explanation of symobls: w = weak, m = medium, s = strong, vs = very strong, br = broad, sh = shoulder.

[a]Arabic numerals are Wilson numbers as assigned for benzene.

[b]Assuming C_{2v} symmetry for nitrogen heterocycles; C_{4v} symmetry for metal-nitrogen modes.

[c]Vibrational assignments; see text for details. Symbols: ν, stretching mode; δ, in-plane bending mode; γ, out-of-plane bending mode; rock = rocking mode; sy = symmetric; as = asymmetric; u = unassigned band.

[d]i = in=phase vibrations; o = out-of-plane vibrations.

[e]Bulk Raman spectra recorded as 1:1 mixture of Cl^-, ClO_4^-, I^-, or PF_6^- salt to KBr or CsI in solid pellet.

[f]chloride salt

[g]perchlorate salt

[h]iodide salt

[i]hexfluorophosphate salt

[j]SER spectra obtained using ca 0.1 - 1 m<u>M</u> complex at roughened silver electrode in either 0.1 <u>M</u> NaBr-or 0.1 <u>M</u> NaCl - based electrolyte (see text for details). For pyridine complexes, electrolyte also contained 0.1 <u>M</u> HCl to suppress hydrolysis. Electrode potentials quoted versus saturated calomel electrode (sce).

[k]Solution contained 10 m<u>M</u> pyridine; 1 m<u>M</u> pyrazine, or 1 m<u>M</u> 4,4'-bipyridine in 0.1 <u>M</u> NaCl.

[l]SER spectra for complex containing pentadeuterated pyridine.

[m]SER spectra for complex containing deuterated ammine ligands; prepared by dissolving complex in neutral D_2O before adding acidified supporting electrolyte.

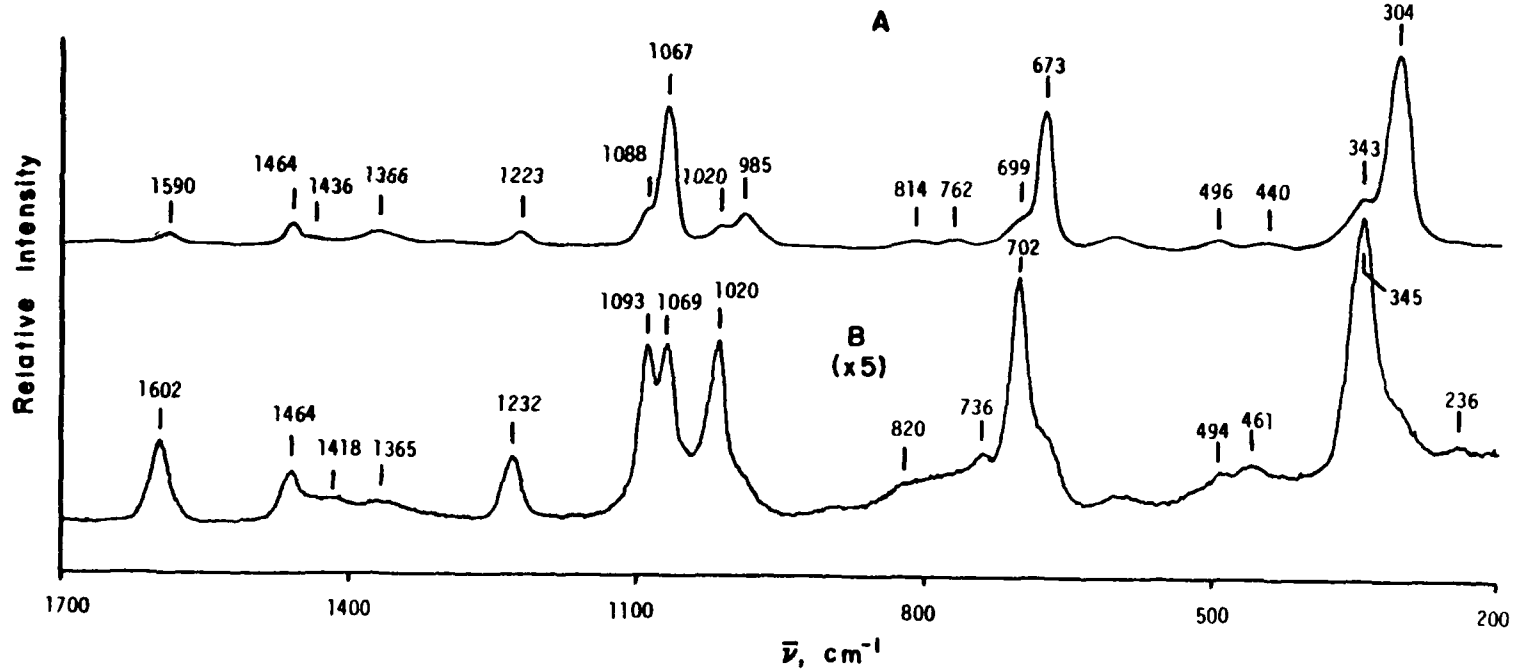
A
1590
1464
1436
1366
1223
1088
1067
1020
985
814
762
699
673
496
440
343
304
B
(x5)
1602
1464
1418
1365
1232
1093
1069
1020
820
736
702
494
461
345
236
Relative Intensity
1700
1400
1100
800
500
200
$\bar{\nu}$, cm^{-1}

Figure Caption

SER spectra in 200-1700 cm^{-1} region for $Os(NH_3)_5pz$ at silver-aqueous interface following oxidation-reduction cycle at (A) -550 mV. (B) -150 mV vs. sce. Solution contained 0.1 mM $Os(NH_3)_5pz^{3+}$ in 0.1 M NaCl. Spectral conditions: 514.5 nm excitation, 100 mW incident power, scan speed 1 cm^{-1} sec^{-1}, time constant 1 sec, resolution 4 cm^{-1}. Note that spectra A is not smoothed, i.e. actual noise level is as shown.